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(54) Title: FUNCTIONAL FLUID

(57) Abstract

Acetals, especially those having from 14 to 25 carbon atoms, especially aliphatic acetals, are used as or in the oil phase of drilling fluids.

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"Functional Fluid"

This invention relates to drilling fluids, more especially to such fluids for use in well drilling.

Drilling of oil or gas wells normally involves the circulation of a fluid through the drill string and out through nozzles in the drill bit, the fluid being returned through the annular passage formed between the drill string and the bore. The fluid cools and lubricates the drill, provides a hydrostatic head to counterbalance pressures, and removes the cuttings from the drill bit. Such fluids are also employed in other areas, for example, geothermal drilling, drilling for water and scientific drilling.

Oil-containing drilling emulsions have been used for many years for these purposes. The emulsion may be in the form of a water-in-oil or an oil-in-water emulsion, in each case normally having finely divided solids suspended therein, and containing a variety of additives for various purposes, e.g., emulsifiers, surfactants, pH control agents, biocides, corrosion inhibitors, weight and viscosity regulators, oxygen and sulphur scavengers, and fluid-loss additives.

The oil traditionally used was a hydrocarbon oil, often with an aromatic content; concern for the environment has recently required hydrocarbon oils used for the purpose to be largely aliphatic and more recently,

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because aliphatic hydrocarbons are not readily biodegradable, hydrocarbons are being increasingly restricted in their use. Many replacements for hydrocarbons have been suggested; these have primarily been aliphatic materials with functional groups that facilitate biodegradation, for example, ester groups. Esters are, however, likely to be saponified in use, causing problems with odour, viscosity increase, wax build up, and poor separation of cuttings from the fluid.

The modern technological and ecological demands on the oil phase components of drilling fluids now make it necessary for the following requirements to be borne in mind. The material should be hydrophobic and of low polarity (to minimize swelling of clays and shales). It should have as high a flash point as possible, advantageously above 100°C, and preferably above 130°C, and more preferably above 160°C. Its viscosity at 20°C should be at most 20 cSt (20 mm²/s), advantageously at most 15 cSt, and preferably at most 10 cSt, and it should have a pour point below -15°C, to be pumpable between -5°C and -10°C. It should be a poor solvent for CO₂ and H₂S. It should remain physically and chemically stable at temperatures up to 250°C, pressures up to 8000 p.s.i. (about 55 MPa) and high pH (up to 10 lb of lime per barrel, about 30 kg of lime per m³ or pH 11) while being biodegradable under aerobic and preferably under anaerobic conditions. The material and its degradation

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products should have low toxicity both to mammals and to marine flora and fauna, and little odour. All these requirements must be met without detracting from the prime purpose of the material, to provide the best possible lubricity.

In EP-A-391251, it is proposed to employ certain water-insoluble ethers as components in water-in-oil drilling fluids.

In EP-A-399270, similar ethers are disclosed for use in oil-in-water drilling fluids.

Such ethers have, however, disadvantages in use in drilling fluids, including being pumpable only with difficulty at temperatures commonly encountered in practice.

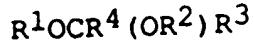
Further, ethers tend to be biodegraded only with difficulty under aerobic conditions.

In EP-A-374671, 374672 and 386638 various esters derived from aliphatic alcohols and acids are proposed for uses in drilling muds but, as indicated above, the stability of esters under the conditions in which drilling muds are used is insufficient.

There accordingly remains a need for a drilling fluid meeting the ecological demands presently being made or likely to be made in the near future.

In the first aspect, the present invention provides the use in the oil phase of a drilling fluid of at least one hydrocarbyl, especially aliphatic, acetal. The

acetal advantageously contains at most 25 carbon atoms, and preferably from 14 to 25 carbon atoms, and more especially is of the formula I



in which R¹ and R², which may be the same or different, represent a hydrocarbyl, especially an aliphatic, advantageously an alkyl or alkenyl, radical with from 3 to 12 carbon atoms, and R³ and R⁴, which may be the same or different, represent hydrogen or a hydrocarbyl, especially an aliphatic, advantageously an alkyl or alkenyl, radical with from 1 to 12 carbon atoms. Again, advantageously, the acetal of the formula I has a total number of carbon atoms of at most 25, preferably within the range of from 14 to 25.

Advantageously, the viscosity of the acetal is at most 20 cSt. (mm²/s) at 20°C.

The term "hydrocarbyl" as used herein means that the radical concerned is primarily composed of hydrogen and carbon atoms but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the radical concerned.

Preferably, in the acetal, R¹ and R² represent alkyl or alkenyl radicals with from 6 to 8, preferably 7, carbon atoms. Advantageously, also, R³ represents an alkyl or alkenyl radical with from 5 to 7, preferably 6, carbon atoms. Advantageously, R⁴ represents hydrogen.

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The total number of carbon atoms is advantageously from 20 to 24 and is preferably 21.

The alkyl or alkenyl groups may be straight or branched chain; if they are branched they advantageously contain methyl and ethyl branches. Alkyl groups are preferred. Mixtures of acetals may be used.

The acetals may be made by methods that are per se known, conveniently by reaction of an aldehyde (less preferably a ketone) with two or more moles of one or more alcohols in the presence of an acid catalyst with heating to distil off the water produced. The synthesis of acetals is described in more detail in "Methoden der Organischen Chemie", Band 6/3, p 109 ff, E. Müller, Ed, G. Thieme Verlag, Stuttgart, Germany.

Alternatively, the acetal may be formed by hydroformylating an aliphatic olefin feedstock, for example a C₆ to C₁₀, especially a C₆ to C₈, feedstock, and hydrogenating the resulting aldehyde. The product contains olefins, saturated hydrocarbons, aldehydes, alcohols and heavy residues. The aldehydes and alcohols are caused to react as described above to form the desired acetal.

Accordingly the invention also provides the use in a drilling fluid of an aliphatic acetal comprising the product obtainable, and advantageously obtained, by hydroformylating an aliphatic C₆ to C₁₀ olefin feedstock, causing the resulting mixture to react in the presence of

an acid catalyst with continuous removal of water, followed by neutralization and stripping; for example with nitrogen, to remove light cuts, e.g., olefins, saturates, and alcohols. This results in a residual product that contains, by weight, 0.5 to 2% alcohols, 3 to 15% ethers, including vinyl ethers, 80 to 90% acetals, and 3 to 9% heavies, the precise percentages depending on the starting oxo feed composition and the reaction conditions.

Advantageously, the hydroformylation is carried out on an olefin feedstock and under conditions appropriate to obtain acetals described above in accordance with the formula I, it being understood that in accordance with this second aspect of the invention the acetals will generally be a mixture of acetals of such a formula, and generally in admixture with other products of hydroformylation and hydrogenation.

The invention further provides a drilling fluid comprising an emulsion having an aqueous phase and an oil phase, in which the oil phase comprises the aliphatic acetal-comprising product obtainable, and advantageously obtained, by the procedures defined above.

The acetal, or mixture of acetals, used in accordance with the invention advantageously has a pour point as determined by ASTM D97 below -15°C, preferably below -20°C and more preferably below -30°C. The acetal, or mixture of acetals, advantageously has a viscosity, as

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determined by ASTM D445 at 20°C, of at most 20 cSt, preferably from 2 to 10, most preferably 3 to 8, cSt mm²/s).

The invention also provides a drilling fluid comprising an emulsion comprising at least one hydrocarbyl, especially an aliphatic, acetal, preferably one having at most 25, more especially from 14 to 25 carbon atoms, advantageously an acetal of the formula I, water, at least one member selected from surfactants and emulsifiers, and at least one member selected from clay, a halide of an alkaline earth or alkali metal, and weighting material.

The emulsion may be an oil-in-water emulsion or, preferably, a water-in-oil emulsion. The working material of the oil phase may consist essentially of an acetal, or may comprise the acetal together with other oils. Advantageously, the acetal constitutes at least 40%, preferably at least 60%, by weight, of the oil phase. Other components may include those conventionally used, for example, the esters of natural or synthetic saturated or unsaturated fatty acids with mono- or poly-functional alcohols, ethers, acetals, optionally alkoxylated amines, ether alcohols, ether acids, ether esters, ether amines, and mineral oils (although these are not preferred for the reasons given above).

When the drilling fluid according to the invention is an oil-in-water emulsion, the oil phase advantageously

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represents from 5 to 65%, preferably from 5 to 50%, more preferably from 5 to 30%, and most preferably from 5 to 10%, by weight, based on the total weight of oil phase and unweighted aqueous phase.

When the drilling fluid is a water-in-oil emulsion, the oil phase advantageously represents from 55 to 95%, preferably from 75 to 95%, and most preferably from 75 to 90%, based on the total weight of oil phase and unweighted aqueous phase.

As indicated above, the drilling fluid advantageously comprises surfactants and/or emulsifiers, groups which to some extent overlap.

As surfactants there may be mentioned, for example, a non-ionic surfactant, for example, polyalkylene ether derivatives of alcohols and alkyl phenols, advantageously having from 3 to 30 alkylene, preferably ethylene, oxy groups and from 8 to 20 carbon atoms in the hydrocarbon chain. Preferably, there are used polyethylene oxy derivatives with from 5 to 20, more preferably from 5 to 15, repeat units with a linear or branched primary alcohol from 8 to 18, more preferably from 10 to 16, carbon atoms in the chain or with an alkyl phenol with a linear or branched alkyl group with from 6 to 14 carbon atoms. Most preferably there is used an ethoxylated fatty alcohol having from 5 to 20, advantageously 7 to 10, ethoxy groups and 11 carbon atoms in the chain which may be linear or branched.

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The surfactant may alternatively be a cationic surfactant, for example an imidazoline derivative, for example a fatty imidazoline salt of a strong monoprotic acid, for example one as described in U.S. Patent No. 3585051, or a quaternary ammonium salt having at least one long chain alkyl or alkenyl substituent, e.g., one having from 8 to 20 carbon atoms, the remaining substituents being alkyl groups with up to 4 carbon atoms, especially methyl, the anion being, for example chloride, bromide, iodide, phosphate, sulfamate, or acetate.

As emulsifier there may be mentioned fatty amine alkoxylates, aromatic alkoxylates or an ether amine alkoxylate. Advantageously, however, the emulsifier is a quaternary ammonium salt, e.g., a long chain alkyl trimethyl or dialkyl dimethyl ammonium chloride, and preferably the quaternized reaction product of an oxyalkylated polyamine with a fatty acid, for example the product of reaction of a soya or coco fatty acid, or a blend of the two, with diethylene triamine, ethoxylation, and subsequent quaternization with methyl chloride.

The drilling fluids of the invention may also contain a viscosity regulator, e.g., clay, for example, bentonite, which may be treated, e.g., with peptizing agents or with organic salts, to render them organophilic. Suitable proportions are, for example, up to 30%, preferably from 5 to 20%, by weight, based on the weight of unweighted aqueous phase and oil phase.

The drilling fluids may also contain weighting agents, for example, barium sulphate, to increase the specific gravity of the fluid, e.g., up to 2.5, and more advantageously up to 1.6.

The drilling fluids may also contain, in the aqueous phase, a soluble alkali or alkaline earth metal salt, especially calcium or potassium chloride, in an amount up to that needed to saturate the aqueous phase.

The drilling fluids may also contain a fluid-loss additive, for example a hydrophobic lignite, to assist in developing a liquid-impervious film on the bore wall. Suitable proportions are, for example, up to 7% by weight, based on the weight of the oil phase.

The following Examples illustrate the invention:

Example 1

Synthesis of C21 acetal from n-heptanal and iso-heptanol
570 g (5.0 moles) of n-heptanal, 1359 g (11.7 moles, 15% molar excess) isoheptanol, 1.9 g (0.01 moles) p-toluene-sulfonic acid monohydrate were mixed in a 3 necked flask equipped with a reflux condenser, Dean-Stark trap, a thermometer and a nitrogen sparging fritted disk. The mixture was heated for 3 hours, 25 minutes, to a final reaction temperature of 110°C under a N₂ flow. A total of 72 g of water was collected in the Dean-Stark trap (79 wt% conversion).

The reaction mixture was neutralized with 19 g Na₂CO₃ at 90°C and five times water-washed at room

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temperature. The product was isolated by nitrogen stripping under a pressure ranging from atmospheric to 100 mm Hg (about 13 kPa) for 12 to 13 hours, to remove the excess alcohol. This treatment resulted in 1386 g of product with a C₂₁ acetal content of 84.2 wt%. The remainder is 2.5% residual iso-heptanol, 11.4% ethers including vinyl ethers, and 1.9% heavies.

Example 2

Synthesis of tri-isooheptylacetel from C₇-oxo hydrofeed

2525 g of C₇-oxo hydrofeed (composition by gas chromatography, per cent by weight: C₆-olefins/saturates 20; isoheptanal 19; isoheptanol 46; hemi-acetals/acetals 6; heavies 9) and 0.5 g p-toluenesulfonic acid are processed as described in Example 1.

A total of 60 g of water was collected in the Dean-Stark trap after 5 hours, 30 minutes, at 74°C. The reaction was continued for another 2 hours at 75°C but under a vacuum of 200 mm Hg (about 27 kPa). An additional 18 ml of water were collected. This corresponds to a 99% conversion of the aldehydes. The product was neutralized with 29 g of sodium carbonate at 90°C.

The product was then stripped under N₂ for ca. 13 hours at 120°C at atmospheric pressure and an additional 2 hours at 135°C under a vacuum of 200-100 mm Hg (about 27 to 13 kPa). This resulted in the removal of the C₆ olefins/saturates and excess of isoheptanol leaving a

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product containing: 0.2 wt% of isoheptanol, 3.4% ethers including vinyl ethers and 88.3% tri-isoheptyl acetal, 8.1% heavies. Finally, the residue was filtered to remove the neutralizing agent and water-washed to yield 1500 g of product.

Example 3

A C₂₁ acetal made as described above was tested for hydrolytic stability. No hydrolysis was observed after storage at room temperature in hydrochloric acid, pH 6, for 23 days or at pH 3 for 13 days, or in calcium hydroxide, pH 14, for 25 days. The acetal was stored in contact with an equal volume of aqueous solution at the given pH.

Results of stability tests at 90°C and 204°C are shown in the tables below.

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Table 1

Days	% Hydrolysis at pH shown	
	pH 3	pH 6
1	6	
2.7		60
5.7		85
6.75	35	
9.7		93.1
9.75	99.96	
12.75	99.99	
13.7		96.8

Table 2. 204°C

Days	% Hydrolysis - pH 14
14	0

The results show that in an alkaline environment such as that encountered in drilling fluids, the acetal is stable even at very high temperatures (important in limestone drilling). In an acid environment, however, the acetal is hydrolysed relatively rapidly. Gas chromatographic analysis indicated that the initial decomposition products were vinyl esters, these being

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converted in turn largely to alcohol and aldehyde. These lower molecular weight products are relatively water soluble and biodegradable.

Example 4

Certain physical properties of the acetals used in accordance with the invention are given in Table 3.

Table 3

Aldehyde Moiety	i-C8	n-C4	n-C7	i-C7	i-C8
Alcohol Moiety	n-C4	i-C8	i-C7	i-C7	i-C8
Carbon Number	16	20	21	21	24
Viscosity, mm ² /s 20°C	4.78	8.84	9.17	12.44	15.16
40°C	2.93	4.84	5.06	6.35	7.45
100°C	1.18	1.68	1.71	1.80	2.11
Flash Point, COC, °C	130	160	152	167	160
Distillation °C, IBP	260.5	216.1	154	247.3	258
50%	280.4	331.4	345	341.1	361.1
95%	287.4	353.4	352.1	394.7	371.3
FPB	379.7	360.3	399.9	413.4	379.7

i-C_n represents iso-alkyl of the given carbon number, where iso indicates the mixed branch product of oxonation. n-C_n represents the corresponding linear alkyl group.

All the acetals listed above had a pour point below -42°C, and were suitable for use alone, or in admixture with other materials, in the oil phase of an oil-in-water or water-in-oil emulsion drilling mud.

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CLAIMS:

1. The use in the oil phase of a drilling fluid of a hydrocarbyl acetal.
2. The use as claimed in claim 1, wherein the acetal has a viscosity at 20°C of at most 20 cSt (20 mm²/s).
3. The use as claimed in claim 1 or claim 2, wherein the acetal has at most 25 carbon atoms.
4. The use as claimed in claim 1 or claim 2, wherein the acetal has from 14 to 25 carbon atoms.
5. The use as claimed in any one of claims 1 to 4, wherein the acetal is an aliphatic acetal.
6. The use as claimed in any one of claims 1 to 5, wherein the acetal is of the formula I
$$R^1OCR^4(OR^2)R^3$$
in which R¹ and R², which may be the same or different, each represents an aliphatic radical with from 3 to 12 carbon atoms and R³ and R⁴, which may be the same or different, each represents hydrogen or an aliphatic radical with from 1 to 12 carbon atoms.
7. The use as claimed in claim 6, wherein R¹ and R² represent an alkyl or alkenyl radical with from 6 to 8 carbon atoms.
8. The use as claimed in claim 6 or claim 7, wherein R³ represents an alkyl or alkenyl radical with from 5 to 7 carbon atoms.
9. The use as claimed in any one of claims 6 to 8, wherein R⁴ represents hydrogen.

10. The use as claimed in any one of claims 1 to 10, wherein the total number of carbon atoms in the acetal is from 20 to 24.

11. The use as claimed in claim 10, wherein the total number of carbon atoms is 21.

12. The use as claimed in claim 6, wherein R¹ and R² represent heptyl, R³ represents hexyl, and R⁴ represents hydrogen.

13. The use as claimed in claim 1, wherein the acetal is obtainable by hydroformylating an aliphatic C⁶ to C¹⁰ olefin feedstock, causing the resulting mixture to react in the presence of an acid catalyst with removal of water, followed by neutralization and stripping to remove light cuts.

14. A drilling fluid having an aqueous phase and an oil phase, wherein the oil phase contains an acetal as defined in claim 13.

15. A drilling fluid comprising an emulsion having an aqueous phase and an oil phase, containing an acetal as defined in any one of claims 1 to 13, water, at least one member selected from surfactants and emulsifiers, and at least one member selected from clay, a halide of an alkaline earth or alkali metal, and weighting material.

16. The invention of any one of claims 1 to 15, wherein the fluid is a water-in-oil emulsion.

17. The invention of any one of claims 1 to 15, wherein the fluid is an oil-in-water emulsion.